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# Ultrasonic and piezoelectric properties of the BT–LMT ceramic system

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**Abstract**

Ultrasonic and piezoelectric studies of lead free ceramic system structures of $(1-x)BaTiO_3$–$xLa(Mg_{1/2}Ti_{1/2})O_3$ (BT–LMT) are presented in this contribution. It was shown, that such materials with $x = 0.025$, 0.05, 0.075 and 0.1 LMT content undergo phase transitions and exhibit piezoelectric effect in the low temperature phases. Anomalies of ultrasonic velocity and attenuation at phase transitions have been observed in these materials. Measurements of temperature dependencies of ultrasonic velocity and attenuation revealed anomalies related to phase transitions in these materials. It was shown that, at room temperature and under dc bias electric field, these ceramics behave as a piezoelectrics because of electrostriction.

*Keywords:* Piezoelectric ceramics; Piezoelectric properties

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## 1. Introduction

Lead-free perovskite relaxors are promising for environment-friendly applications in electroacoustic devices.[1] A number of relaxors have been derived from barium titanate (BT).[2] Low-loss dielectric perovskite $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) was found to be an appropriate end member to form relaxor compositions based on BT. Particular solid solutions of the BT–LMT systems were recently prepared. It was shown that BT ceramics doped with 2.5 mol.% of LMT exhibit the typical features of both the ferroelectric and the relaxor,[3] while BT–10% LMT demonstrates solely the relaxor properties.[4] Dielectric investigations of BT–LMT performed by the macroscopic methods (averaging over many grains) and on the nanoscale level (in a single grain) have proved the presence of polar nanoregions in the ceramics at temperatures above the dielectric permittivity peak.[4,5] Recently, homogeneous ceramics $(1-x)BaTiO_3$–$xLa(Mg_{1/2}Ti_{1/1})O_3$ ($(1-x)$BT–$x$LMT) with the compositions $x = 0.025$, 0.05, 0.075 and 0.1 were obtained. The X-ray diffraction studies[6] have revealed the tetragonal (*P*4*mm*) perovskite structure for the compositions with $x < 0.025$ and the cubic (*Pm*3*m*) for $x > 0.05$ at the room temperature. The relaxor state in the $(1-x)$BT–$x$LMT system appears when three ferroelectric phase transitions (as in pure BT) merge into one diffuse transition at $x > 0.05$. At the same time, the $(1-x)$BT–$x$LMT ceramics acquire the relaxor features continuously with growing $x$. The continuous crossover from ferroelectric to relaxor behavior observed in $(1-x)$BT–$x$LMT was explained by a cluster model of relaxors. Usually relaxors, e.g PMN-PT, are the strong piezoelectrics and exhibit electrostriction-induced piezoelectricity at room temperature.[7] Therefore, it is of great interest to study the elastic and piezoelectric properties of the BT–LMT ceramic system. In this contribution, we present the results of experimental ultrasonic and piezoelectric investigations of BT–LMT ceramics with different compositions. Investigation of the temperature dependencies of ultrasonic attenuation, velocity and piezoelectric properties revealed the anomalies at diffuse phase transitions. The electrostriction-induced piezoelectric effect was observed at room temperature in the BT–LMT ceramic plates.

## 2. Experimental

Ceramic BT–LMT samples with LMT composition 0.025, 0.05, 0.075 and 0.1 were prepared and characterized in University of Aveiro according to the methods described in.[5] Ultrasonic velocity and attenuation measurements were carried out using the computer controlled pulse-echo equipment.[8,9] The ultrasonic system allowed us to measure delay intervals less than 0.2 ns, therefore the precise relative ultrasonic velocity measurements were possible. The piezoelectric measurements were performed using the custom-made automatic

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resonance–antiresonance system.[9–12] Calibration of the absolute sound velocity at required stabilized temperature was performed by precise measurement of the electromechanical antiresonance frequencies. Silicone oil was used to make acoustic bonds and silver paint electrodes were used in electric measurements.

## 3. Results and discussion

The ultrasonic velocity and attenuation measurements were carried out in BT–LMT ceramic samples, cut from rectangular bars and polished so that two opposite sides were parallel. The sample length along the longitudinal ultrasonic wave propagation direction was about 0.5 cm. The absolute values of the ultrasonic velocity and attenuation values at the room temperature were determined from the delay times and amplitudes of three consecutive reflected echo pulses with a 2% precision. Next, we measured the temperature variation of delay time and amplitude only of first echo. Dependencies of ultrasonic velocity $v$ and attenuation $\alpha$ were measured at the frequency 10 MHz in a cooling run. The ultrasonic velocity decreased with decreasing temperature and attained broad minima (Fig. 1). For BT–LMT with 2.5% LMT, there are two broad minima in the velocity dependence, which can be attributed to the phase transitions, first from the rhombohedral phase to the orthorhombic one in the vicinity of $T_1 = 220$ K, and next to the tetragonal phase near $T_2 = 250$ K. The velocity anomaly that is related to the tetragonal–cubic phase transition merges to the one close to $T_2$. Nevertheless, the broad attenuation ($\alpha$) peak that is related to this transition is seen at $T_3 = 290$ K (Fig. 2). From such ultrasonic behaviour (broad elastic anomalies shifted to lower temperatures) one can conclude that the phase transitions in this 2.5% LMT ceramic compound are already influenced by internal strains and exhibit relaxor features. With increasing of the LMT content, the dependencies $v = f(T)$ and $\alpha = f(T)$ shift to lower temperatures, but the two broad attenuation peaks for $x = 0.05$ can be still resolved. For compounds with $x > 0.05$, the only one minimum in ultrasonic velocity and relevant attenuation maximum remain, indicating pure relaxor behaviour. Thus, from ultrasonic measurements the conclusion of gradual crossover from ferroelectric to relaxor behaviour in BT–LMT ceramics[5] was confirmed.

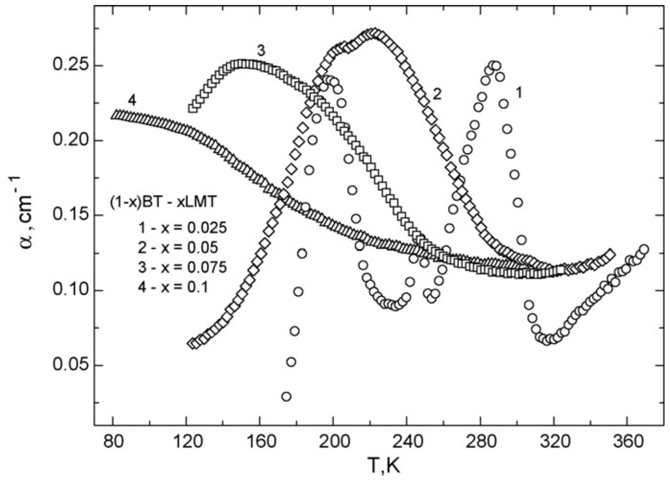

Fig. 2. The temperature dependencies of longitudinal ultrasonic attenuation measured in unpolarised BT–LMT ceramics at 10 MHz frequencies.

By direct measurements of the electric signal amplitude ($U$) from BT–LMT piezoelectric transducer it was shown that the piezoelectric effect exists in ceramics with compositions $0.025 < x < 0.1$ in temperature range below 312 K (Fig. 3). In this experiment, the exciting 10 MHz lithium niobate transducer was attached to the one end of the quartz buffer, and the thin BT–LMT plate was glued to the other end (see ref. 12 for details). The plate was cut from the same bar, which was used in ultrasonic experiments. Measurements were carried out in heating run after poling the ceramic samples at $T > 350$ K. The temperature dependence of the signal detected by such transducer roughly represents the temperature dependence of piezoelectric modulus of the BT–LMT plate. For 2.5% LMT ceramic, the two anomalies at $T_1 = 220$ K and $T_2 = 260$ K can be seen. The signal vanishes at the temperature above 350 K. Such behaviour corresponds to that of

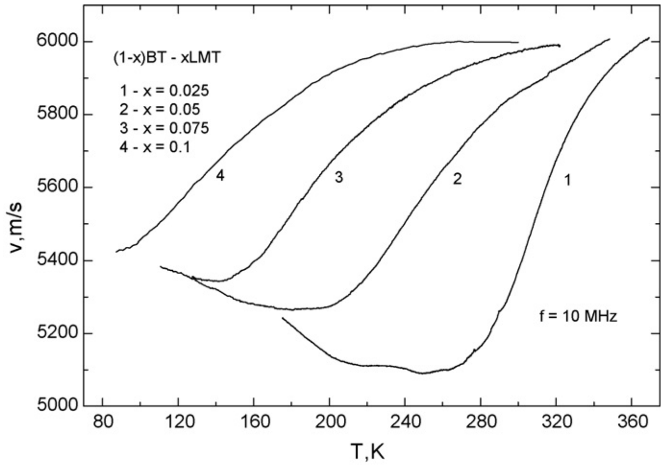

Fig. 1. The temperature dependencies of longitudinal ultrasonic velocity measured in unpolarised BT–LMT ceramics at 10 MHz frequencies.

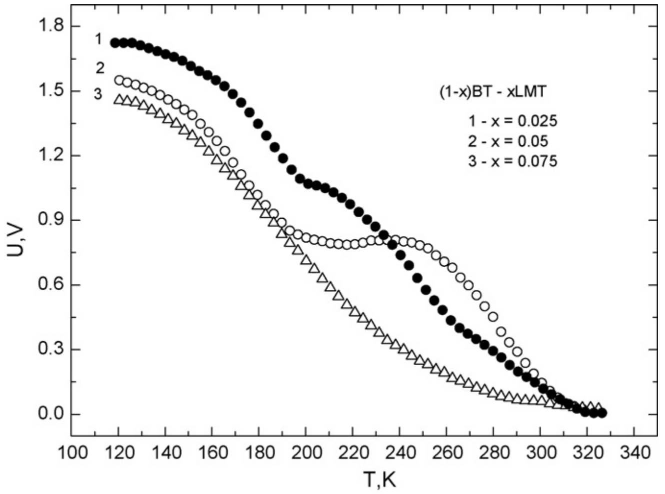

Fig. 3. The temperature dependencies of amplitude of electric signal detected by BT–LMT ceramic plates.

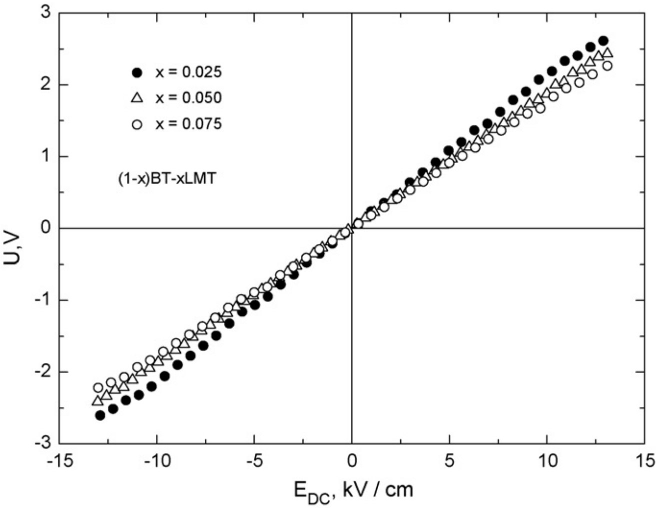

Fig. 4. The dependencies of electric signal amplitude detected by BT–LMT plates with different composition on dc bias electric field.

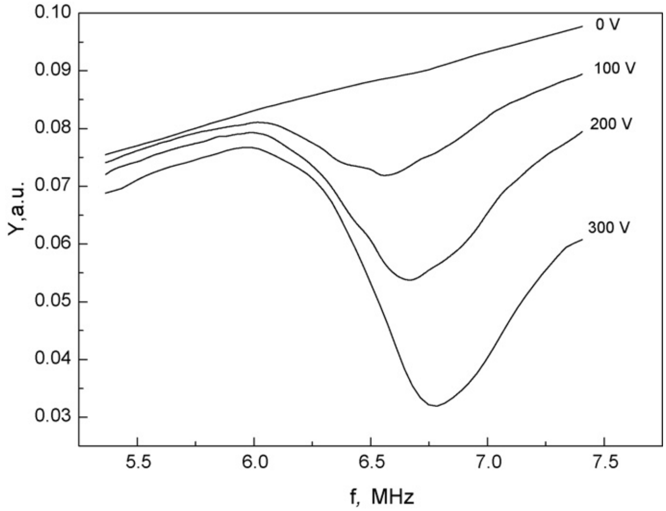

Fig. 6. Evolution of electric admittance in various dc bias fields for BT–LMT ceramic plate at room temperature.

ultrasonic velocity and attenuation and represents the sequence of three phase transitions in 2.5% LMT compound. For ceramics with $x = 0.05$ the change of the slope and the saturation of detected piezoelectric signal were observed near 220 K, where the saturation in ultrasonic velocity takes place (see Fig. 1). For ceramics with $x = 0.075$ only the gradual increase of the detected ultrasonic signal with decreasing temperature can be seen in Fig. 3 (curve 3), what indicates a complete evolution from ferroelectric to relaxor properties. As one can also see from Fig. 3, the electromechanical conversion at room temperature is very small for all investigated BT–LMT ceramic materials. This situation became different when the dc electric field was applied to the BT–LMT plates. In this case, plate operated as ultrasonic transducer and the 10 MHz ac voltage appeared, which grew with increasing the dc field. Hence, we observed the electrostriction-induced piezoelectricity in these ceramic materials (Fig. 4). The negative values of voltage ($U$) only show the change of the polarization direction in a sample. By reversing the dc electric field, the phase of the detected 10 MHz signal changed by 180°. This was clearly seen on the screen of an oscilloscope displaying the RF pulse. It should be noted, that the signal amplitude ($U$) detected by the BT–LMT electrostrictive ultrasonic transducer in a dc electric field is time-dependent: it slightly increases with time (Fig. 5). We attribute such behaviour to the migration and reorientation of defects or polar nanoregions, which can be related to memory effects observed earlier in other ceramic materials.[13,14] The redistribution of free charges also can lead to the changes of the effective dc field, which is responsible for the electrostriction-induced piezoelectric effect. The electrostriction-induced piezoelectric behaviour was also confirmed by the conventional resonance–antiresonance method. The frequency spectra of ceramic planar transducers were measured and resonance–antiresonance character was observed in the frequency dependencies of electric admittance $Y$. The evolution of electric admittance modulus ($Y$) in various dc bias fields is shown in Fig. 6 for 2.5% LMT ceramics. It was possible to calibrate the electromechanical parameters of such electrostrictive transducers by determining the resonance and antiresonance

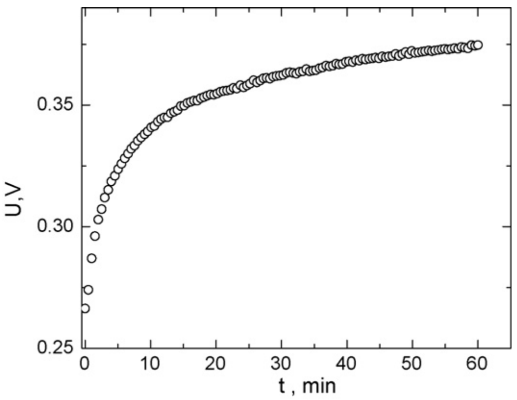

Fig. 5. The time dependence of ultrasonic signal amplitude detected by BT–LMT plate. The applied dc field was 10 kV/cm.

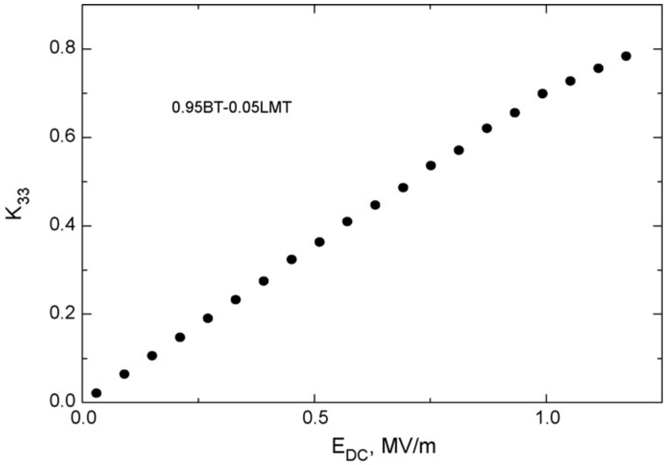

Fig. 7. The variation of electromechanical coupling coefficient of BT–LMT ceramic on dc bias electric field.

frequencies from Fig. 6. The electromechanical coupling coefficient for given thickness vibration mode was calculated from the equation

$$K_{33}^2 = \frac{\pi f_r}{2 f_a} tg \left( \frac{\pi}{2} \frac{f_a - f_r}{f_a} \right) \quad (1)$$

After such a calibration, the field dependencies of $K_{33}$ could be readily obtained from data of the pulse-echo measurements (see Fig. 6). We note that the signal should be proportional to $K_{33}$. The typical dependence $K_{33} = f(E_{dc})$ is shown in Fig. 7. The values of the electromechanical coupling coefficient $K_{33}$, in large dc bias fields near breakdown, are of order 0.7–0.8, and can be compared to $K_{33}$ values in polarised BT–LMT ceramic materials at low temperatures. This suggests possible applications of materials studied for implementation dc voltage controlled ultrasonic transducers.

## 4. Conclusions

The temperature dependencies of longitudinal ultrasonic velocity and attenuation in BT–LMT ceramics revealed anomalies, which are indication of phase transitions in these materials. The composition dependencies of the ultrasonic anomalies reflect the evolution from ferroelectric to relaxor behaviour. The electrostriction induced piezoelectric effect was observed in BT–LMT ceramics at room temperature and the dependencies of electromechanical coupling coefficient on the dc bias field for longitudinal excitations were measured. We have shown that the thin plates of BT–LMT ceramics can effectively excite and detect ultrasonic waves.

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